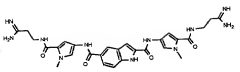
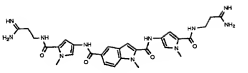
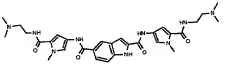


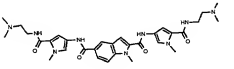
1



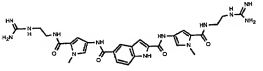
2



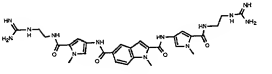
3



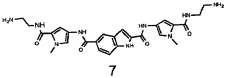
4



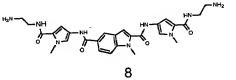
5



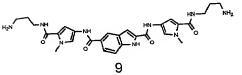
6



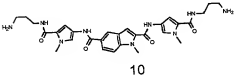
7



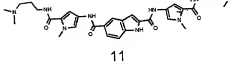
8



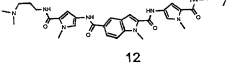
9



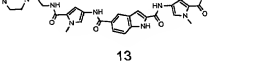
10



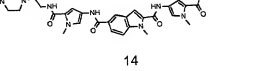
11



12

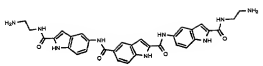


13

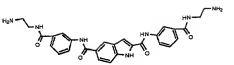


14

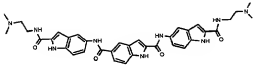
FIG. 1



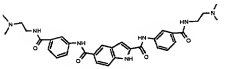
14



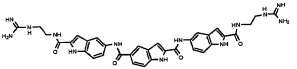
16



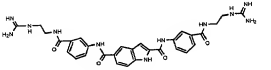
17



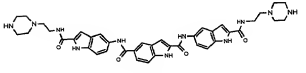
18



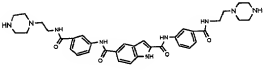
19



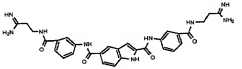
20



21



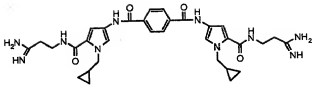
22

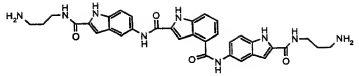


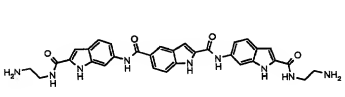
23

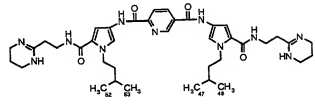
FIG. 2

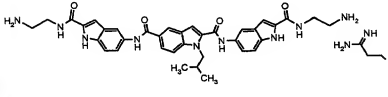
FIG.3

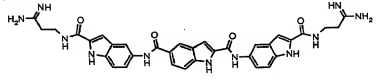


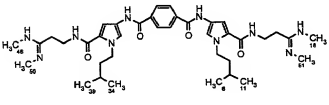


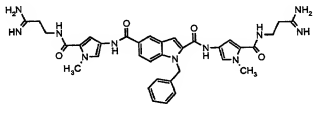


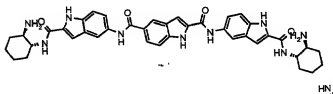


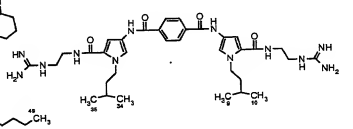


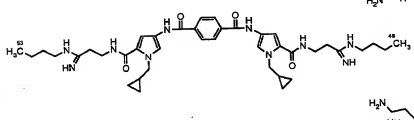


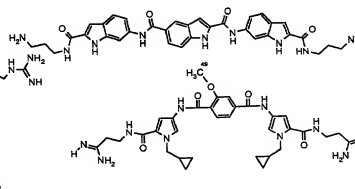


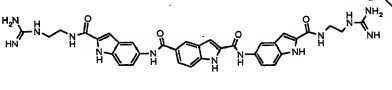












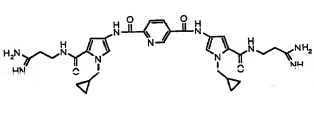
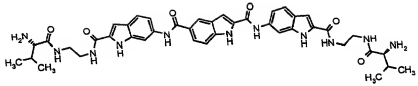
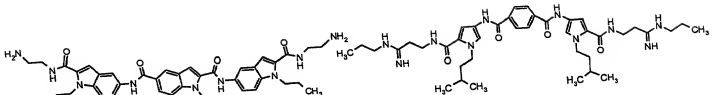
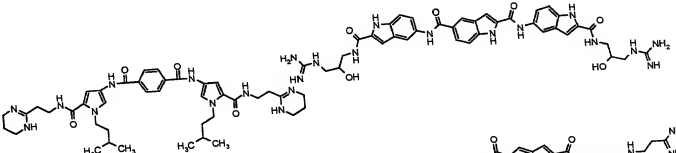
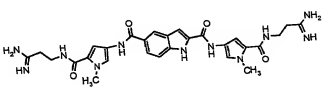


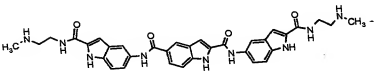
FIG. 4

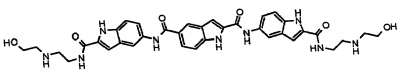


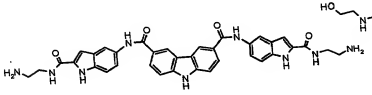


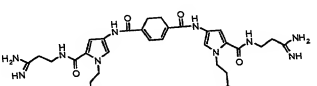


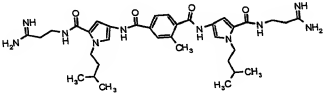












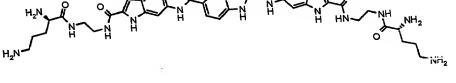
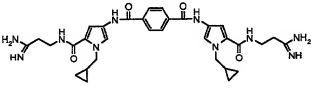
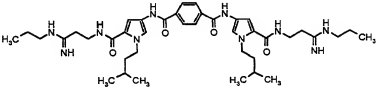
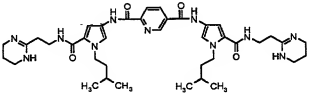
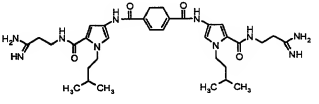


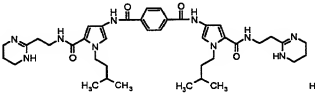
FIG.5

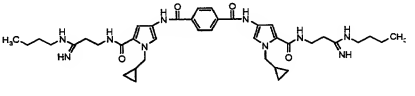


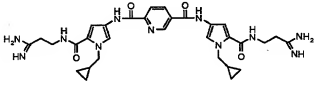


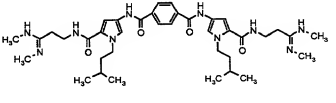


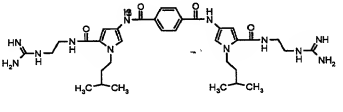


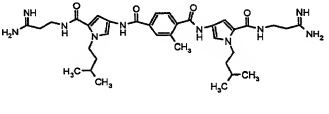












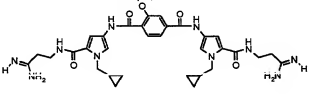
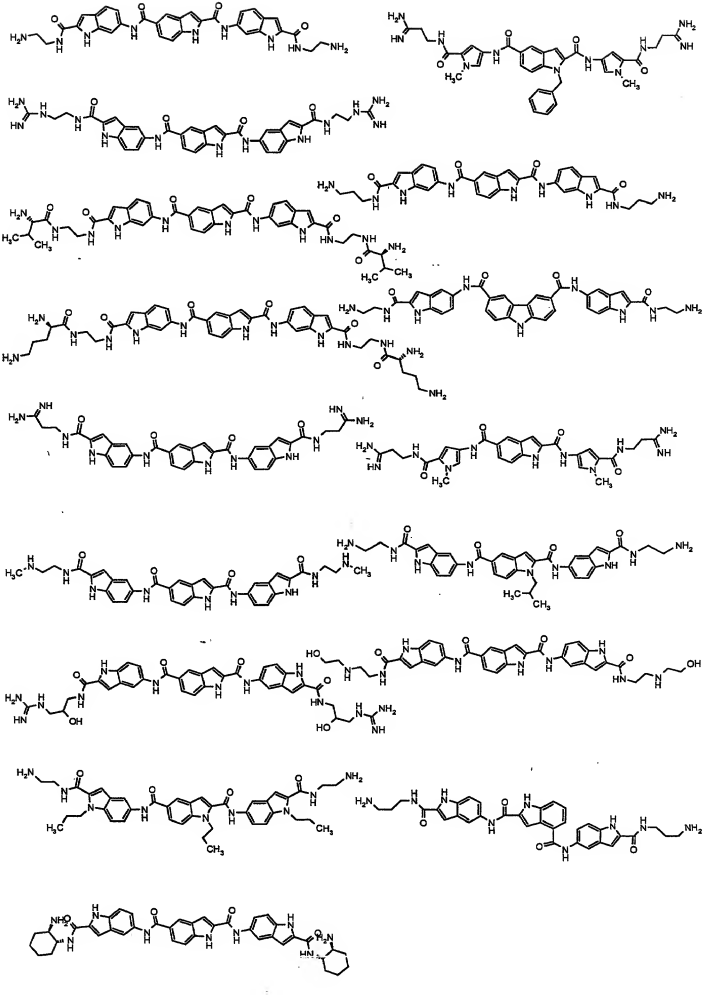
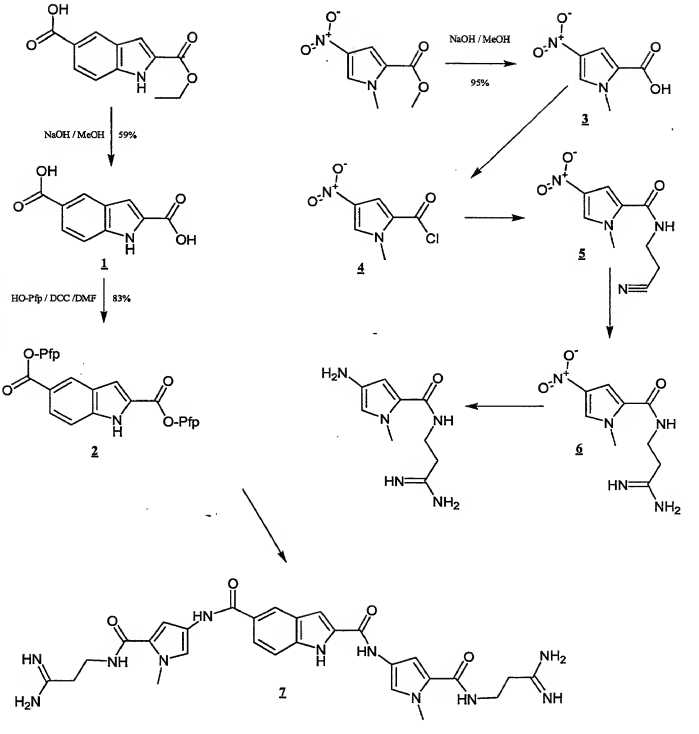


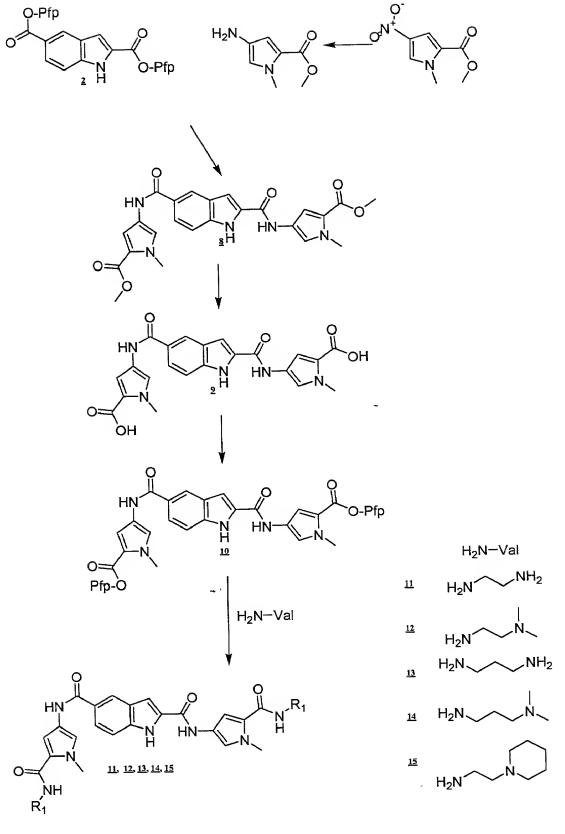
FIG. 6



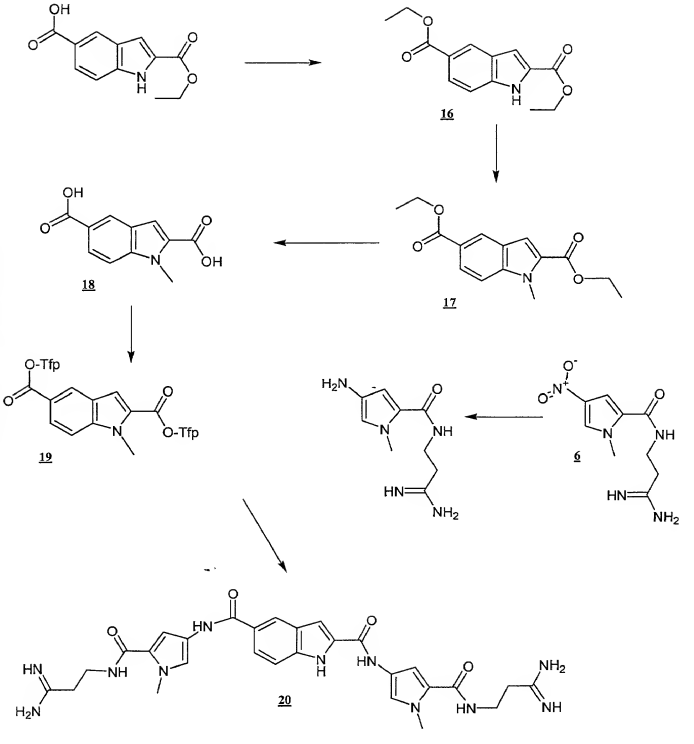
Scheme 1



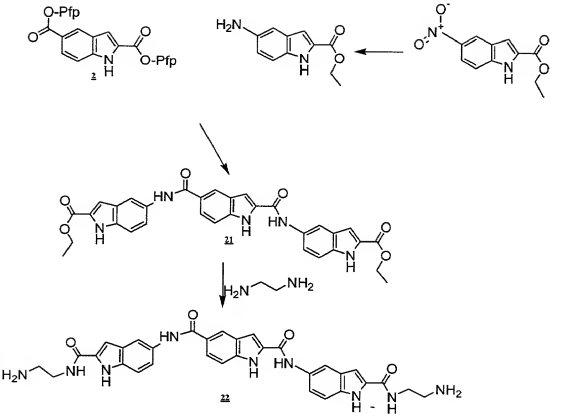
Scheme 2


O-Pfp
O-Pfp
2
H2N
HN
N
H
8
9
OH
10
Pfp-O
H2N–Val
11, 12, 13, 14, 15
R1
NH
H2N–Val
11
12
13
14
15

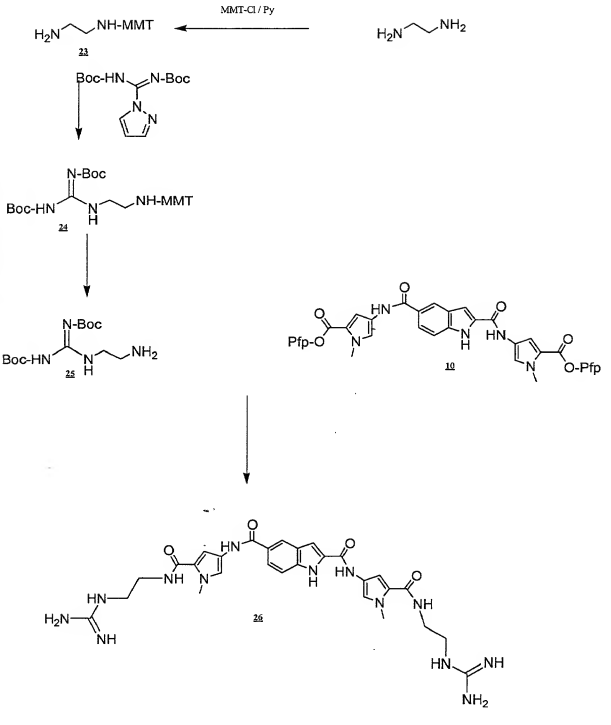
Scheme 3

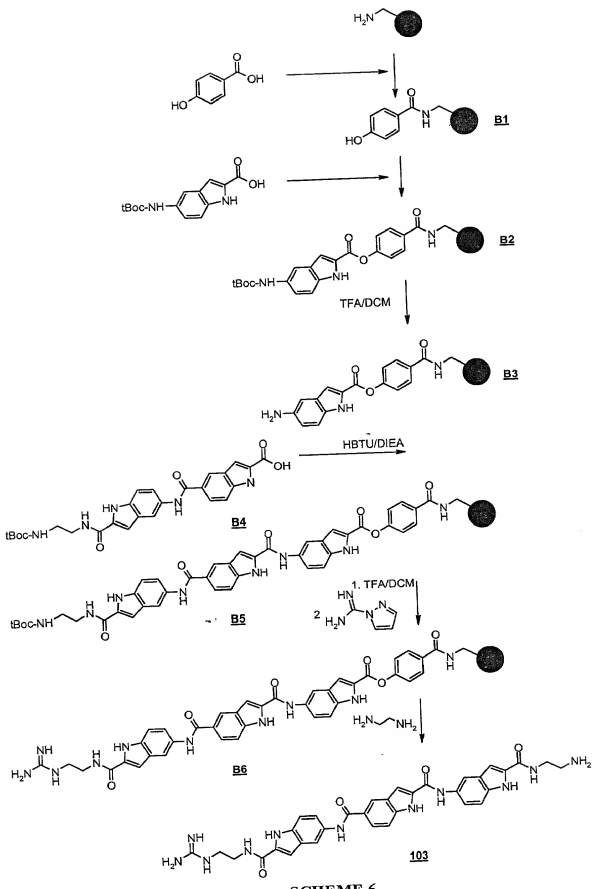


Scheme 4

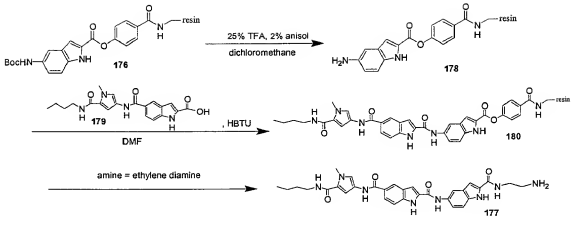


Scheme 5

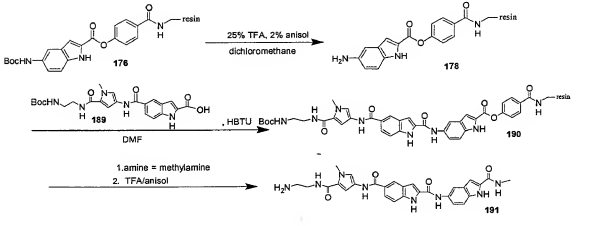

MMT-Cl / Py
H2N
NH-MMT
23
NH2
Boc-HN
N-Boc
24
25
Pfp-O
O-Pfp
10
26
HN
NH
NH2



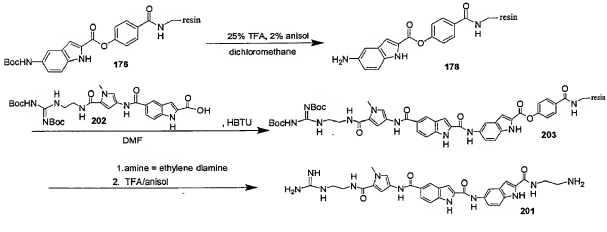
SCHEME 6



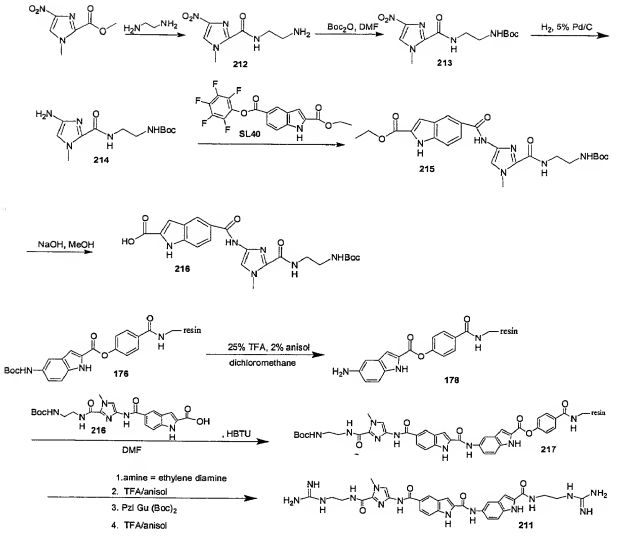
SCHEME 7



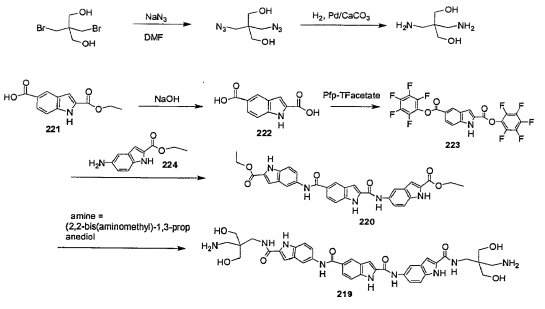
SCHEME 8



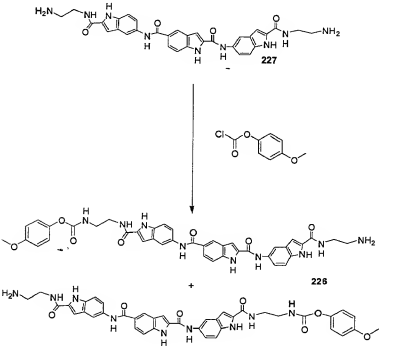
SCHEME 9


Boc2O, DMF
H2, 5% Pd/C
212
213
214
SL40
215
NaOH, MeOH
216
25% TFA, 2% anisol
dichloromethane
176
178
DMF
HBTU
217
1.amine = ethylene diamine
2. TFA/anisol
3. Pzl Gu (Boc)2
4. TFA/anisol
211

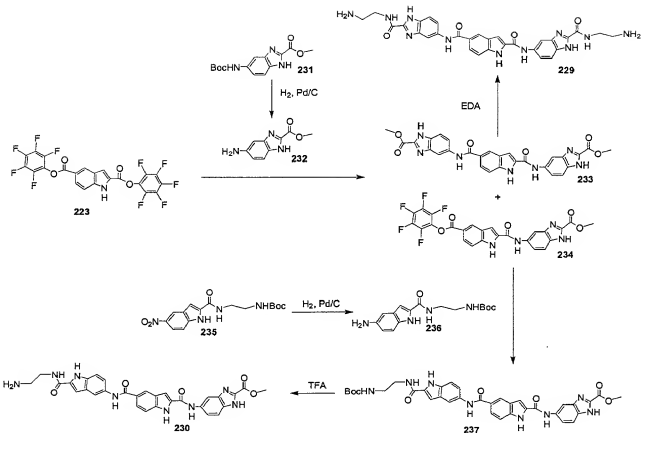
SCHEME 10



SCHEME 11



SCHEME 12


BocHN
231
H2, Pd/C
H2N
232
223
EDA
229
233
234
O2N
235
H2, Pd/C
H2N
236
NHBoc
TFA
BocHN
237
230

SCHEME 13